



Review

Catalytic ozonation in water: Controversies and questions.

Discussion paper



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ABSTRACT

The aim of this work is to point out a number of controversies in the results of research on catalytic ozonation, discuss them and indicate their possible reasons. The existing literature has provided many quite well documented proposals of possible mechanisms of catalytic ozonation. However, a closer analysis of all these proposals reveals that many of them are simply contradictory. The number of controversies in the field of catalytic ozonation may indicate our poor understanding of the mechanisms of the process. It is also possible that the reasons for the controversies lie in some basic experimental errors.

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1. Introduction

The term “catalytic ozonation” is used in both air and water purification. The process of catalytic ozonation for air purification is widely known and well described not only from theoretical point of view but also from that of practical applications [1].

The intention of using a catalytic ozonation in water or wastewater treatment is to improve the efficiency of ozonation. The process may be realized in homogeneous and heterogeneous modes. In homogeneous mode, the ions dissolved may be

responsible for catalytic effects. In heterogeneous mode, a variety of solids has been shown to be catalytically active. Despite years of research catalytic ozonation has not been applied widely in water industry. There are only single industrial applications in France and China [2,3], however the results of the applications have not been published so far. There are many claims of catalytic activity observed on a laboratory level – however there are no results of up scaling of the processes. The reason is probably a poor understanding of the process. Mechanisms of catalytic ozonation of aqueous solutions are not easy to investigate mainly due to the presence of overwhelming quantities of H₂O molecules. The aim of this work is to point out the number of controversies in the results of research on catalytic ozonation, discuss the controversies and identify some typical experimental errors that are partly responsible for such a situation. The paper is not aimed at criticism of particular papers

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and my intention was rather to try and show some problems that should be seriously solved by the scientific community.

2. Catalytic ozonation – advanced oxidation process

Catalytic ozonation is expected to:

- generate hydroxyl radicals particularly at lower pHs (or other reactive oxygen species),
- control the radical generation to increase the efficiency of ozonation,
- mineralize water pollutants (also NOM) at higher efficiency, mainly due to increased mineralization of carboxylic acids, typical ozonation by-products,
- lead to higher efficiency of ozone consumption,
- avoid bromate formation.

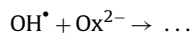
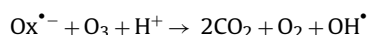
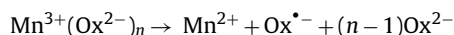
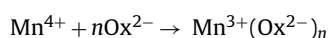
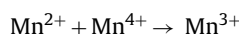
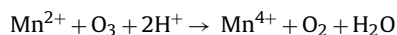
Catalytic ozonation is often classified as an advanced oxidation process, i.e. it is expected that catalytic ozonation will generate hydroxyl radicals. Already at this level of basic expectation some controversial results have been published in literature. It appears the catalytic activity does not necessarily mean generation of hydroxyl radicals and there are many examples of such activity in relevant literature without generation of radicals. Thus, how to classify catalytic ozonation? We can talk about the catalytic ozonation when the efficiency of ozonation in the presence of a catalyst is higher than without it at the same pHs. However when investigating catalytic activity of a solid catalyst, also another condition must be fulfilled, the total effect of catalytic ozonation must be higher than a combined effect of adsorption on the catalyst surface and ozonation alone at the same pHs. As we can see the measurements of pH in both ozonation alone and catalytic ozonation are basic requirements which allow a separation of two effects: decomposition of ozone (and perhaps formation of OH^\bullet radicals which is highly pH dependent) and catalytic activity. In a number of papers concerning the catalytic ozonation these conditions have not been fulfilled and thus many results presented in literature are not fully reliable [4].

2.1. Homogeneous phase catalytic ozonation

Some transition metal cations have been shown to improve ozonation efficiency. There are many homogeneous catalytic systems described in literature. Some of them are collected in Table 1. A variety of different mechanisms has been proposed by the authors to explain the observed effects. The systems have been investigated at different pHs and that is why the proposals are difficult

to compare. However I will try to find out common features of the mechanisms proposed.

According to Sánchez-Polo et al. [15], some metal cations (Fe(II) , Ni(II) , Zn(II) Mn(II) and Cr(III)) would enhance formation of hydroxyl radicals when ozonated, while other cations would not (Sr(II) , Cu(II) , Cd(II) and Hg(II)). In homogeneous phase in the presence of Fe(II) ions, ozonation proceeds with the formation of hydroxyl radicals. On the other hand, ozonation of oxalic acid in the presence of Co(II) proceeds with the formation of Co-oxalic acid complex and then ozone attacks the complex. According to the mechanism proposed by Pines and Reckhow [6] ozone molecule reacts with a neutral CoC_2O_4 complex. This mechanism has been confirmed by Beltrán et al. [7]. In another work, Beltrán et al. [8] have also shown that in the presence of Fe(III) . The ozonation of oxalate proceeds also without formation of hydroxyl radicals, however in this case ozone reacts with both negatively and positively charged complex moieties. In both cases (Co and Fe) hydroxyl radicals are formed as secondary by-products. There are also many contradictory views on the catalytic effects observed in $\text{Mn}^{2+}/\text{O}_3$ systems. In one of the earliest reports on Mn^{2+} catalytic activity Andreozzi et al. have explained the mechanism of the catalytic effect as related to the formation of Mn(III) complex with oxalate ions, generation of oxalate ionradical [16] and simultaneous reduction of Mn(III) to Mn(II) . Further, the ionradical is attacked by molecular ozone and that leads to formation of hydroxyl radicals. They proposed the following reactions chain:



In the views of some authors Mn^{4+} is responsible for the oxidation of the acid [9], other consider formation of unstable Mn^{3+} and the presence of oxalate as necessary for the formation of OH^\bullet radical [12,13]. Also Andreozzi et al. considered system $\text{Mn(II)/oxalic acid}$ as a catalytic [17].

The common features in all these systems are listed below.

Table 1
Homogeneous catalytic ozonation. Proposed mechanisms.

Catalytic system	Reaction responsible for catalytic effect	Comment	pH	Ref.
$\text{Fe}^{2+} + \text{O}_3$	Formation of OH^\bullet			[5]
$\text{Co}^{2+} + \text{O}_3 + \text{oxalate}$	$\text{CoC}_2\text{O}_4 + \text{O}_3$	t-BuOH does not influence the reaction		[6,7]
$\text{Fe}^{3+} + \text{O}_3 + \text{oxalate}$	$\text{Fe}(\text{C}_2\text{O}_4)_2 + \text{O}_3$	Less efficient than with Co^{2+}		[8]
	$\text{FeC}_2\text{O}_4 + \text{O}_3$			[8]
$\text{Mn}^{2+} + \text{O}_3 + \text{pyruvate}$	$\text{Mn}^{4+} + \text{pyruvate}$	Ozone oxidizes Mn^{2+} to Mn^{4+}	2–4	[9]
$\text{Mn}^{2+} + \text{O}_3 + \text{atrazine}$	Formation of OH^\bullet	t-BuOH strongly influences the reaction	7.0	[10]
$\text{Mn}^{2+} + \text{O}_3 + \text{oxalate}$	No catalytic effect		7.5	[11]
$\text{Cu}^{2+} + \text{O}_3 + \text{oxalate}$	Catalytic effect	No discussion concerning mechanism	7.5	[11]
$\text{Mn}^{2+} + \text{O}_3 + \text{DNT}$	No catalytic effect		5.5	[12]
$\text{Mn}^{2+} + \text{O}_3 + \text{oxalate} + \text{DNT}$	Catalytic effect $\text{Mn}^{2+} + \text{O}_3 + \text{H}^+ \rightarrow \text{Mn}^{3+} + \text{OH}^\bullet$	Oxalate reduces Mn^{3+} to Mn^{2+} OH^\bullet detected by ESR/spin-trap Carbonate hinders catalytic effect	5.5	[12]
$\text{Mn}^{2+} + \text{O}_3 + \text{DCP}$	OH^\bullet formation	Oxalate is formed as a by-product of DCP ozonation	5.5	[13]
$\text{Mn}^{2+} + \text{phenol} + \text{O}_3$	No catalytic effect	pH not specified		[14]

DNT – dinitrotoluene, DCP – dichlorophenol.

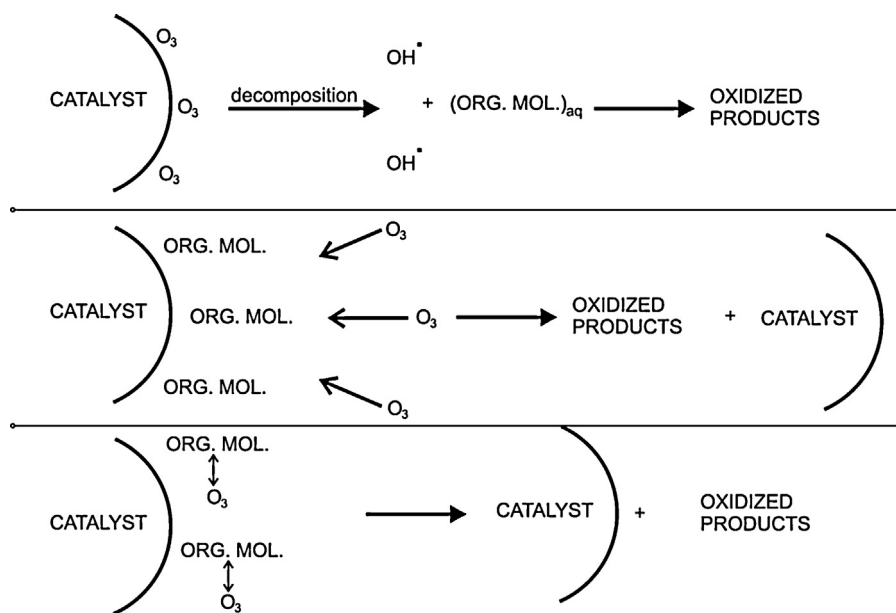


Fig. 1. Three possible cases of heterogeneous catalysis.

- All of them are based on transition metals that can oxidize and reduce back to the initial form,
- In all the systems some formation of complex between the acid (oxalate, pyruvic) seems to be necessary for the catalytic effect (the acid may be a product of a direct ozonation of the organic molecule), however, the results shown in [11] are still controversial about that,
- There are two reactions: (primary) in a simple system ozone attacks the complex of Me-acid, and the reaction leads to the formation of OH^\bullet that can react (secondary) with more complicated molecules (that is why in some simple systems the catalysis does not depend on radical pathway but for higher molecular weight molecules secondary radicals are vital for the process).

It remains to explain whether the ozone may equally efficiently attack neutral, and positively and negatively charged metal-complex species.

The above described system would explain the possible mechanism for most of the cases described as homogeneous catalytic ozonation.

2.2. Heterogeneous catalysis

In heterogeneous catalytic ozonation catalyst is in a solid form while the reaction may proceed in bulk water or on the surface of the catalyst. We can talk about the catalytic ozonation when the effect of ozonation in the presence of a catalyst is higher than a combined effect of adsorption on the catalyst surface and ozonation without a catalyst at the same pHs. In many cases the formation of hydroxyl radicals is expected to be responsible for the catalytic effects. The catalytic effect is possible when at least one of the three conditions is fulfilled (Fig. 1):

- ozone is adsorbed on the surface of the catalyst,
- organic molecule is adsorbed on the surface of the catalyst,
- or both, ozone and organic molecule are adsorbed on the catalyst surface.

The catalytic effect cannot be expected when none of the reactants is adsorbed on the catalyst surface.

A variety of solid catalysts has been described in literature as effective for ozonation of organic molecules in aqueous solutions. The catalysts belonging to the following groups are mainly used:

- metal oxides,
- metals supported on oxides,
- minerals,
- activated carbon.

2.3. Metal oxides

Various metal oxides are claimed to show catalytic activity in ozonation. The main group element oxides (Al_2O_3) and transition metal oxides (TiO_2 , Fe_2O_3 , MnO_2) have been proved to be catalytically active. Surface chemistry of all the oxides seems to be quite similar: the surface is covered by hydroxyls that can have ion-exchange properties and the hydroxyls are considered as the main adsorption centers. Some of the oxides may have also Lewis acid centers on their surfaces. Other oxides may have also hydrophobic sites which could have some affinity to less polar organic molecules.

Different hydroxyls may be found on the oxide's surfaces: single (or isolated) hydroxyl sites are the most popular on silica but also a variety of other oxides may bear such sites on their surfaces. Bridged (and also tribridged) $M-(OH)-M$ hydroxyls seem to be another group of hydroxyl sites which are characteristic of alumina, zirconia and titania. The hydroxyls are also main ion-exchange sites. The ion-exchange properties depend on pH of the surrounding environment. Thus the oxides may exchange cations at pH higher than oxides' pH_{pzc} and anions at pHs lower than their pH_{pzc} . A detailed discussion of the adsorption of organic molecules on oxide surfaces the reader may find in review papers [18–21]. In general, adsorption of organic compounds on metal oxide surfaces depends on polarity of the former. The strongest adsorption can be expected for organic ions, however their adsorption depends on pH. Polar compounds may get adsorbed on the surfaces, while nonpolar organics are not adsorbed on the surfaces unless some hydrophobic sites are present there (e.g. in high silica zeolites).

Lewis acid sites are usually found on dry metal oxides such as alumina, zirconia, titania. These sites are extremely reactive and they react dissociatively with water molecules. Thus, in aqueous interphase conditions, the sites are usually blocked by water

Table 2The mechanisms of catalytic ozonation proposed for MnO_2 .

Catalytic system	Reaction responsible for catalytic effect	Comment	pH	Ref.
MnO_2 + oxalic acid + O_3	Formation of surface MnO_2 –oxalic acid complex, ozone reacts with the complex	The highest reactivity at pH 3.2	3.2–7	[31]
MnO_2 + pyruvic acid + O_3	(Ozonation alone – the same results)	No catalytic effect	2–4	[9]
MnO_2 + atrazine + O_3	Adsorption of solute on <i>in situ</i> MnO_2 not assessed	The effect similar to homogeneous catal. ozonation in the presence of Mn^{2+}	7	[32]
MnO_2 + propionic acid + O_3	No effect	No cat. effect at pH 6.8	pH 1 pH 6.8	[33]
MnO_2 + sulfosalicylic acid (SSal) + O_3	MnO_2 –SSal surface complex + O_3	Slight effect at pH 1	pH 1	[33]
MnO_2/GAC + nitrobenzene + O_3	Catalyst decomposes ozone, TBA does not influence the cat. ozonation	OH^\bullet radicals are not responsible for the catalytic effect		[34]
MnO_2/GAC + oxalic acid + O_3	Formation of surface MnO_2 –oxalic acid complex, ozone reacts with the complex	OH^\bullet radicals are not responsible for the catalytic effect	pH 3	[63]

molecules. Lewis acid sites may also coordinate molecules of Lewis bases and that explains for instance a high affinity of the oxide surfaces to phosphate, sulfate, fluoride and carboxylic anions [22,23].

Some oxides, particularly high silica zeolites, may contain hydrophobic surface that enhances adsorption of organic compounds.

The catalytic ozonation literature is full of contradictory reports on catalytic activity of oxides. Many metal oxides are used in catalytic air purification [1,24] and it has been shown that p-type oxides such as MnO_2 , NiO , Co_3O_4 , Fe_2O_3 , Ag_2O and CeO_2 are particularly active in ozone destruction [1]. Some of them are claimed to be catalytically active also in catalytic ozonation in aqueous solutions [25–27]. In 2003 Pines and Reckhow [28] reported that metal oxides do not decompose ozone molecules into hydroxyl radicals. However, since then many papers have been published that claim the ability of oxides to catalyze the decomposition of ozone molecules. On the other hand, the success of catalytic ozonation may be connected with the ability of oxides to form surface complexes. Below, a few exemplary mechanisms of heterogeneous catalysis on metal oxides in ozonation of aqueous solutions are discussed.

2.4. MnO_2

Dry MnO_2 was shown to dissociatively adsorb ozone molecules to form oxygen and atomic oxygen species [29,30] however traces of water were proved to hinder the process. In many literature reports, manganese dioxide is also claimed to be catalytically active in aqueous ozonation. The authors of the reports have proposed different mechanisms of its catalytic activity. The suggested mechanisms are collected in Table 2.

According to Ma and Graham [32] only MnO_2 generated *in situ* is catalytically active while commercial samples of manganese dioxide are not.

Here again the formation of surface MnO_2 /oxalic acid complex is necessary to observe catalytic activity of MnO_2 , but no such activity has been observed for pyruvic acid [9] or propionic acid [33] (pyruvic acid $\text{pK}_a = 2.39$ [35], propionic acid $\text{pK}_a = 4.86$). According to Tong et al. [33] the ability of different forms of MnO_2 to decompose ozone in aqueous solution does not necessarily mean that manganese dioxide is an effective catalyst for the decomposition of organic compounds. Recently Orge et al. [63] have confirmed the mechanism proposed earlier by Andreozzi et al. [31]. According to [63] adsorbed oxalic acid is attacked by molecular ozone.

2.5. Al_2O_3

There exists a variety of views on a catalytic activity of alumina. For some researchers, alumina is an active catalyst while for others alumina does not reveal any catalytic activity. First of all it is absolutely necessary to emphasize here the necessity of pH

measurements when experimenting with alumina, particularly when the substrate is of commercial origin. Alumina is often produced by an alkali precipitation from aluminum salts and it may contain residuals that change pH to higher values. Thus all the papers in which pH of the reactions was not measured should be disqualified. The first report on ozone decomposition by alumina appeared in 1999 [36] and in this very paper the authors did not measure the value of pH. We have recently shown that impurities of commercially available alumina may considerably increase the pH of water and may lead to observation of false catalytic effect [37]. According to Lin et al. [38] alumina does not decompose ozone, and our measurements [39,40] confirmed that. The lack of ozone decomposition does not necessarily mean the lack of catalytic effect, but two views have been put forward. According to the results observed by our group [41] for the catalytic effect, adsorption on the surface is necessary. The same has been observed by Álvarez et al. [42] for catalytic ozonation of pyruvic acid. According to two other reports (Ernst et al. [43] and Beltrán et al. [44]) the adsorption of organic molecule seems to be detrimental to catalytic effect. Therefore, to observe the catalytic activity without adsorption of organic molecule, the adsorption of ozone on the alumina surface would be necessary. As we can see these are two contradictory views on the catalytic activity of Al_2O_3 .

Another controversial issue regarding the catalytic activity of alumina is the catalytic mechanism. In most of the papers the exact catalytic mechanism is not discussed only the effect is observed. In those papers the authors *a priori* assume that if the effect is observed then generation of hydroxyl radicals must occur. In view of the above discussion and also in view of new achievements in this field [45–47], it seems to be clear that hydroxyl radical formation is not absolute necessity for observing catalytic activity.

2.6. Fe-hydroxyoxides

Even stranger and full of controversy is the attitude to the catalytic activity of iron hydroxyoxides. According to two papers of Park et al. [48,49], FeOOH decomposed aqueous ozone to hydroxyl radicals and the reaction between organic solutes and the radicals took place on the surface or in the interphase (depending on pH). According to Beltrán et al. [8] catalytic ozonation of oxalic acid on $\text{Fe}_2\text{O}_3/\text{Al}_2\text{O}_3$ surface proceeds via the reaction of molecular ozone and surface oxalic complex. Another possibility has been presented by Zhang and Ma [50], according to them decomposition of ozone on goethite into hydroxyl radicals proceeds on neutral (undissociated) surface hydroxyls. Finally, the fourth hypothesis concerning catalytic activity of iron hydroxyoxides has been presented by Sui et al. [51]. According to them ozone molecules are stronger Lewis bases than phosphates and the formation of hydroxyl radicals proceeds on Lewis acid sites available on the goethite surface.

Table 3
Mechanisms of catalytic ozonation suggested for Fe hydroxyoxides.

Catalytic system	Reaction responsible for catalytic effect	Comment	pH	Ref.
FeOOH + O ₃	OH [•] in interphase	Ozone and pCBA adsorption on FeOOH	2 < pH < 7	[52]
FeOOH + O ₃ + pCBA	Ozone reaction with surface	No OH [•] radicals involved	pH 2.5	[8]
FeOOH + O ₃ + FeOOH + O ₃ + nitrobenzene	Complex of oxalic acid with Fe ₂ O ₃	Formation of OH [•] radicals at neutral pH	pH ≈ 7	[50,53]
FeOOH + O ₃ + OxA	Decomposition of ozone on non-dissociated hydroxyls	Neutral and positively charged hydroxyl groups are responsible for ozone decomposition with formation of OH [•]	pH 4pH 7	[51]
	Adsorption of ozone on Lewis sites			

Summarizing: we have four papers concerning one catalyst and four different mechanisms responsible for the catalytic activity. All of the papers are well documented and when read separately they all seem to be reasonable. However, there are four different hypotheses and all of them cannot be true. This example shows irrefutably that our understanding of the catalytic ozonation seems to be very poor. Table 3 presents four different mechanisms of catalytic ozonation on Fe hydroxyoxides.

2.7. Metals supported on oxides

Metals supported on metal oxides (or carbon) have also been shown to decompose ozone into hydroxyl radicals. The exact mechanism is not known but two possible routes have been proposed by Legube and Karpel Vel Leitner [25]: the first one comprises adsorption of organic molecule on the catalyst surface, then its oxidation by ozone or hydroxyl radical and desorption of the oxidized product; the second route comprises generation of OH[•] by the oxidation of reduced form of metal by ozone, adsorption of organic molecule, its oxidation by an electron transfer, and desorption of the product with simultaneous reduction of metal site. Both routes were proposed at very early stage of research on catalytic ozonation and in general the hypotheses have not been proved so far. Fonatnier et al. [2] published in 2005 a very significant paper concerning the mechanism of catalytic ozonation, however the details of the catalyst composition have not been revealed. According to the paper, metals supported on inorganic supports were used. The mechanism of the catalysis suggested by Fonatnier et al. [2] indicated formation of a very reactive complex between metal and ozone followed by the reaction of the complex with organic molecule in the solution. No generation of hydroxyl radicals was noted. This is therefore another example illustrating that catalytic ozonation does not necessarily rely on hydroxyl radical formation.

2.8. Active carbon

There is also a variety of mechanisms proposed to explain the catalytic activity of active carbons (in fact active carbon surface can act rather as an initiator/promoter of ozone decomposition since ozonation modifies its surface chemical properties):

- O₃ decomposes on the surface of AC [54]; OH[•] are formed and react with organics in bulk solution,
- Ozone is adsorbed on AC surface at acid and near neutral pHs and no OH[•] are generated; at 6 < pH < 9 O₃ the decomposition proceeds and is catalyzed by OH[•] groups adsorbed on AC surface [55],
- At pH 2.5 mineralization of oxalic acid proceeds via radical pathway in solution [56],
- At pH 3 the reactions occur on the AC surface and in the solution [57] – basicity of AC is responsible for O₃ decomposition (confirmed also by Sánchez-Polo and Rivera-Utrilla [58]),

- AC catalyzed ozonation leads to formation of hydrogen peroxide (Gu et al. [59]),
- Adsorbed diclofenac and ozone react on the surface of AC (Beltrán et al. [60,61]), formation of H₂O₂ has been confirmed,
- Adsorbed O₃ decomposes on AC with a formation of active oxygen species (O[•], OH[•]), they can react with both adsorbed and dissolved organics. Two routes of ozone decomposition are proposed: (i) AC acts as an initiator of O₃ decomposition into hydroxyl radicals and (ii) ozone reacts with surface groups, generates adsorbed H₂O₂ and it reacts with ozone in bulk solution yielding OH[•] radicals [62].

This sequence of hypotheses concerning the mechanism of ozone decomposition mechanism on active carbon surface may reflect the changing view on the mechanism as the subsequent hypotheses are on the one timescale. However, what is bothering the author is the amounts of AC applied in particular papers. E.g. Jans and Hoigné [54] used only 0.1 g/L of AC while the authors of the other papers used even as much as 40 g/L of AC to observe the catalytic effect.

2.9. Typical experimental errors

It seems that some of the controversies in catalytic ozonation have been caused by simple experimental errors.

1. *Lack of proper pH control.* When the experiment concerns the catalytic decomposition of ozone, the results must be compared with the decay of ozone in water at the same pH. It is not necessary to remind that ozone decomposition strongly depends on pH. It seems to be easy to assure the same pH in both experiments but usually researchers have failed to control pH after introducing the catalyst into water (or water with corrected pH e.g. with acid or pH stabilized with buffer). Introducing a catalyst into water may dramatically change the pH value. There are several reasons for that, of which the most important is the presence of mineral impurities in the catalyst. Therefore a strict control of pH is advised particularly after introducing a catalyst into water, during the process of catalytic decomposition of ozone and just after finishing the experiment. One should remember that the highest unwanted changes in pH may be expected for relatively neutral solutions as very low concentrations of acid or base would substantially change it.
2. *Adsorption of substrate on the catalyst surface.* Ozonation alone may destroy the organic compound to some extent. After introduction of the catalyst to aqueous solution of the compound, the organic may also get adsorbed on the catalyst surface and therefore some additional decay of the compound would be observed. The difference obviously is not in the catalytic ozonation but in the adsorption. Therefore the catalytic ozonation effect is observed when the total effect of the ozonation in the presence of the catalyst is higher than the combined adsorption and ozonation alone effects.

3. *Adsorption of the products of ozonation.* Sometimes some summary parameters such as TOC or COD are used to describe the catalytic ozonation effects instead of a decay of the particular compounds. Ozonation alone is used for reference. There is a possibility that by-products of single ozonation may be adsorbed on the catalyst surface. Then the effects observed for the ozonation alone and “catalytic” ozonation would be different. But the reason for the difference is adsorption of the ozonation products on the catalyst surface and not the catalytic effect. It is easy to overcome such a trap, one should perform a single ozonation, measure TOC (COD) then add the catalyst, stir, leave the mixture for the same time as used for catalytic experiment (without ozone) and measure the parameters again. The results should indicate the extent of adsorption of the ozonation by-products on the catalyst surface.
4. *Realistic ratio of catalyst to organic substrate.* In any practical application the organic substrate: catalyst ratio is much higher than unity. It is therefore unacceptable to use grams of the catalyst to show the catalytic activity to micrograms of the organic compounds. When a catalyst is used in huge excess relative to the organic substrate, the catalytic activity may be connected with unknown (also unrealized) impurities in the catalyst. Even several repetitions of the process on the same batch of catalyst may be affected by impurities. Moreover in such systems, the effects of adsorption of the main compound or its ozonation by-products may be easily overlooked.
5. *Purity of the catalyst.* Many commercially available materials are used as ozonation catalysts such as active carbons, alumina, titania and many others. These materials are not pure substances and they contain a variety of impurities. Laboratory made substances are not free from impurities however it is easier to control them. More catalyst means more contaminants and thus stronger impurity effects may be expected. The impurities may substantially change pH and again the higher the concentration of catalyst, the more difficult it is to control pH. The lower the ratio of organic substance to catalyst, the higher the influence of contaminants on the catalytic effect. Contaminants of the catalyst may substantially change the catalyst surface properties (e.g. alkali impurities in active carbons apparently increase the carbon pH_{pzc} [4]). If the impurities of the catalyst are responsible for the catalytic effect one cannot expect any long run activity.
6. *“One run” catalysts.* It is obvious that the catalytic activity must be confirmed in many runs on the same batch of the catalyst. The catalyst which is active in one or two runs does not deserve more attention as its “catalytic” activity is probably caused by some impurities or it reacts with the substrate. It is therefore necessary to show catalytic activity in several repetitions on the same batch of the catalyst or in a continuous system. Continuous systems seem to be much better as any industrial application should work in such a mode.
7. *Natural water conditions.* It is obvious that any perspective catalyst should work with water containing all the natural constituents. Therefore after initial experiments confirming catalytic activity in model solutions the catalyst should confirm its activity in natural water (containing expected concentrations of cations (Ca^{2+} , Mg^{2+} etc.), anions (HCO_3^- , Cl^- , SO_4^{2-}), and NOM).

2.10. The peculiarities concerning the mechanism of catalytic ozonation

1. Presence of water in the system. We have emphasized in our 2010 review [27] that the presence of water in the catalytic ozonation mechanism cannot be underestimated or neglected. Discussing the adsorption properties of many catalysts one cannot neglect the adsorption of water on metal oxides or minerals

surfaces. Discussing the catalytic ozonation mechanism one cannot also forget about the overwhelming amounts of water.

2. It is necessary to point out that in heterogeneous catalysis, particularly when metal oxides are used as catalysts, the acidic centers (Brønsted or Lewis) are often considered responsible for ozone decomposition. In general, we all know that acidic environment rather stabilizes ozone. As pointed out in above both types of acid sites on metal oxides are expected to be well covered with layers of adsorbed water. Contrary to metal oxides the basic sites on active carbons are considered responsible for ozone decomposition. Thus, this view is in agreement with the stability (or rather instability) of ozone in water. Therefore, the question arises: should acid sites be responsible for the ozone decomposition on metal oxides while in active carbons basic sites are responsible for the same. Is not it weird?
3. Metal oxides surfaces are quite similar: all of them bear hydroxyls on the surface, all of them may strongly adsorb water, all of them may be charged depending on their pH_{pzc} and therefore they may reveal anion or cation exchange properties depending on pH. I would not therefore expect any basic differences in catalytic mechanisms on different oxides (if any catalytic effects are proven without doubt). However some metals in transition metal oxides may be oxidized and reduced (e.g. $\text{Fe}^{2+}/\text{Fe}^{3+}$; or $\text{Mn}^{3+}/\text{Mn}^{4+}$) contrary to e.g. Al.
4. In gas–solid catalytic system a problem of catalyst “poisons” is well known. Poisons are compounds that may be detrimental to the catalytic activity. In catalytic aqueous ozonation literature there are almost no reports on catalysts poisons.

3. Conclusions

Hundreds of papers concerning catalytic ozonation have appeared in literature over the last 20 years and we still do not have any unified mechanism of the process. Moreover there have been no up-scaling attempts of the process and almost no industrial applications. There are a variety of papers in which authors do not discuss their results with the existing proposals of mechanisms and do not try to compare their results with others. In other words a serious discussion of the proposed mechanisms is lacking. After years of research on the catalytic ozonation much more conclusive results should be expected. In fact, we may even argue if the catalytic ozonation is a radical process or not. May we classify the catalytic ozonation as an advanced ozonation process or not? The aim of the paper was to show the number of controversies concerning the mechanisms of catalytic ozonation in water. Part of the problems may be a result of some experimental errors which should be avoided in future. Another part of the problems is a discussion which does not refer to reality, e.g. the neglect of the overwhelming presence of water.

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